

ABIOTIC SYNTHESIS OF HYDROCARBONS ON MARS: THEORETICAL MODELING OF METASTABLE EQUILIBRIA. M. Yu. Zolotov¹ and E. L. Shock², ¹Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130; Vernadsky Institute Russian Academy of Sciences, Kosygin St. 19, Moscow 117975, e-mail: zolotov@zonvark.wustl.edu, ²Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, e-mail: shock@zonvark.wustl.edu.

Introduction: The ALH84001 martian meteorite contains polycyclic aromatic hydrocarbons (PAHs) and other hydrocarbons (HC) of endogenous origin [1-4]. McKay et al. [1] have proposed that the presence of PAHs in carbonate globules of ALH84001 indicates biological activity on ancient Mars. On the other hand, HC in other meteorites, IDPs, interstellar clouds, in Earth's pristine and altered igneous rocks (e.g., serpentinites) are not attributed to biological sources. In many cases these HC are formed abiotically due to reduction of carbon oxides by hydrogen. Here we used thermodynamic calculations of metastable equilibria to evaluate the possibility of abiotic synthesis of PAHs and *n*-alkanes in possible hydrothermal fluids and thermal gases on Mars.

Model: Hydrocarbons are thermodynamically unstable compounds and may form if the formation of stable methane or graphite is inhibited [e.g., 5]. On Mars and Earth, this inhibition could have happened in dynamic cooling systems: volcanic/impact gases, fumaroles, and hydrothermal systems around magmatic intrusions or hot impact craters. We considered metastable equilibria among condensed PAHs and *n*-alkanes with gaseous and aqueous CO₂ and H₂, which could have existed in these systems on ancient Mars. In addition, we considered some aromatization and PAH methylation equilibria. We assume that the fugacity (*f*) of H₂(gas) and activity (*a*) of H₂(aq) are controlled by the quartz-fayalite-magnetite (QFM) or hematite-magnetite (HM) buffers, which represent martian igneous rocks and oxidized soil/sediments. We use 5.4 mbar and 1 bar for *f*CO₂, which correspond to the present and a possible ancient atmosphere. In the terrestrial analogy, for carbonate-bearing hydrothermal systems we use *f*CO₂ values that are governed by calcite-silicate equilibria (eqs. (4-7) in [6]). We assumed the activity of condensed HC and water are unity. Pressure corresponds to liquid - water vapor saturation. The thermodynamic data for unsubstituted and methylated PAHs and *n*-alkanes (carbon number 5-20) are from [7] and [8] respectively.

Results: The calculated activities/fugacities of H₂ and CO₂ for the following metastable equilibria:



are plotted in Figs. 1-3 as saturation lines. PAHs and *n*-alkanes can be formed if these *a* and *f* exceed the metastable equilibria values. Saturation lines for PAHs and *n*-alkanes lie close to each other, therefore, the formation of a metastable mixture is more likely.

At the *f*H₂ controlled by the QFM buffer the saturation conditions for HC match with the *f*CO₂ conditions pro-

posed for Mars (Fig. 1). However, the HM buffer is too oxidized to stabilize HC.

A decrease in temperature facilitates the condensation of HC (Fig. 2,3). At the QFM buffer and CO₂ governed either by the CaCO₃-bearing systems or atmospheric CO₂ PAHs and *n*-alkanes can be metastably formed below 90-180°C. Light PAHs can condense together with heavy alkanes. More reduced conditions and higher CO₂ abundance raise the condensation temperatures. In addition, possible high-temperature quenching of H₂ (see dotted line in Fig. 3) increases the condensation temperatures and facilitates HC synthesis.

High temperature and/or oxidizing conditions favor aromatization of *n*-alkanes (Fig. 4). At QFM, aromatization can proceed above ~170°C.

Calculations of equilibria for methylation reactions for PAHs show that low temperature and reduced conditions favor alkylation of parent compounds. At QFM and <~350°C, methylated PAHs are more stable than the unsubstituted species.

Discussion: The predominance of mafic and ultramafic rocks on Mars would favor high *f*H₂ in magmatic gases and high *a*H₂ in aqueous solutions formed during the alteration of these rocks (e.g., serpentinization). High CO₂ contents proposed in martian thermal systems favor the synthesis of HC and, in addition, provide high (*a*,*f*)CO₂ owing to high temperature CO-CO₂ equilibrium. In dynamic systems, C-O-H gases may quench below 300-700°C and produce higher disequilibrium amounts of CO and H₂, which favors the Fischer-Tropsch (FT) type synthesis of HC. The FT synthesis and the proposed CO₂-H₂ interaction could be catalyzed by magnetite [9,10] in igneous rocks and the martian regolith.

Conclusion: Thermodynamic analysis of metastable equilibria show that PAHs could be formed abiotically together with *n*-alkanes in dynamic cooling gaseous (volcanic/fumarolic/impact) and aqueous geothermal systems on Mars below ~180°C. Reduced compositions, high initial temperature of gases/fluids, and quick quenching facilitate the synthesis of HC. However, the oxidized martian regolith and O₂-bearing subsurface fluids do not favor such synthesis.

The possibility of joint formation of PAHs and *n*-alkanes indicate that these HC in ALH84001 could be formed in a single process. Our calculations for the aromatization and methylation equilibria also support the suggestions of Anders [11] that magmatic or impact heating on Mars could increase the PAH content and drive their dealkylation.

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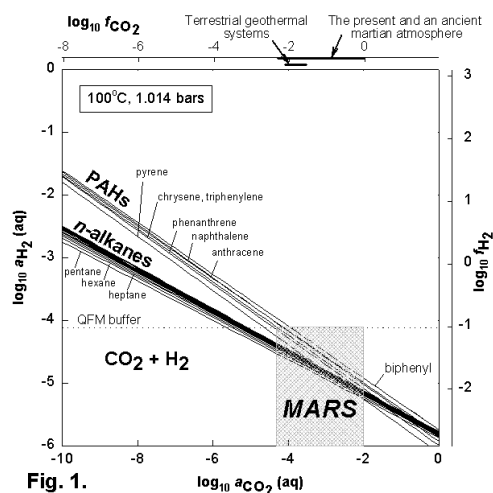


Fig. 1. The metastable equilibrium saturation lines for PAHs and *n*-alkanes at 100°C. The shaded box represents the proposed conditions in martian thermal systems.

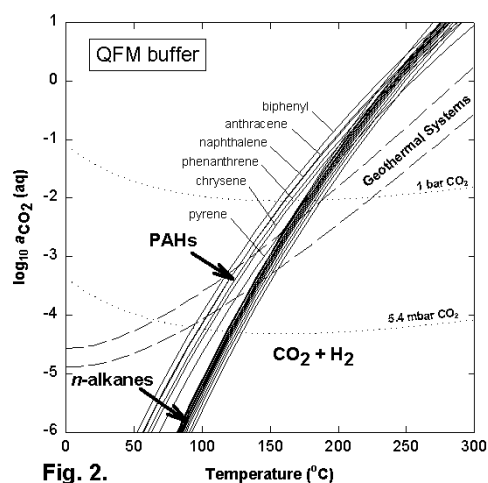


Fig. 2. The metastable equilibrium saturation lines for HC at the QFM buffer. Dashed lines show CO₂ in terrestrial [6] and proposed martian geothermal systems. Dotted lines show *a*CO₂

equilibrated with the present and possible ancient atmosphere of Mars.

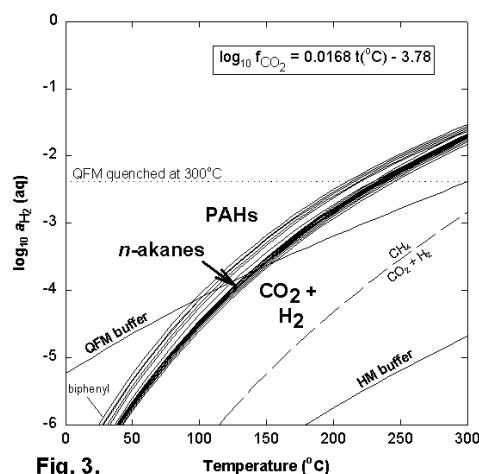


Fig. 3. The metastable equilibrium HC saturation lines at the CaCO₃-silicate equilibria (eq. (7) in [6]).

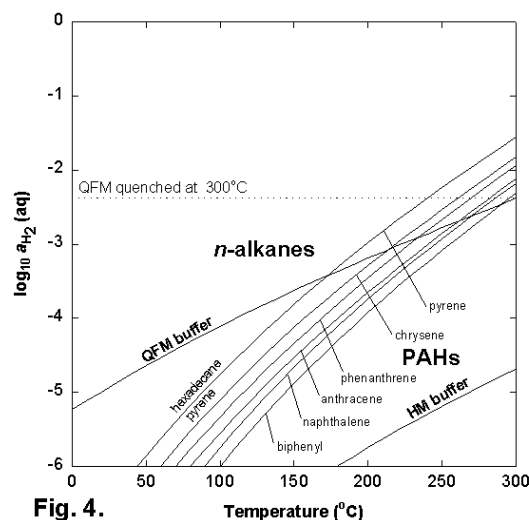


Fig. 4. The metastable equilibrium conditions between pairs of *n*-alkanes and PAHs with the same carbon number as a function of log *a*H₂ and temperature. The hexadecane to pyrene curve is indicated, other curves are labeled by the PAHs.